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(54) CATHODE ACTIVATING MATERIAL OF LITHIUM SECONDARY BATTERY AND PRODUCTION THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a cathode activating material with improved cycle characteristics, especially charging and discharging cycle characteristics, at a temperature as high as 40-70°C and provide a method for producing such a cathode activation material.

SOLUTION: This cathode activation material for a lithium secondary battery is a mixture of a chalcogen compound of at least one element selected from Ge, Zn, Pb, In, Sb, Bi, and Zn and a Li-Mn type compound oxide and is produced by heating both components of the chalcogen compound and the Li-Mn type compounded oxide at 200-900°C in the mixed state. A lithium secondary battery using this cathode activation material has excellent charging and discharging cycle characteristics especially at a high temperature about 60°C.

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CLAIMS

[Claim(s)]

[Claim 1] Positive active material for lithium secondary batteries characterized by consisting of mixture of the chalcogen compound of at least 1 element and Li-Mn system multiple oxide which were chosen from the element group which consists of germanium, Sn, Pb, In, Sb, Bi, and Zn.

[Claim 2] Positive active material according to claim 1 whose chalcogen compound is $\text{Li}_r\text{M}_1\text{M}_2\text{pO}_q$ ($0.5-1.5q$ are [at least 1 element chosen from the group to which M1 consists of germanium, Sn, Pb, In, Sb, Bi, and Zn here, at least 1 element chosen from the group which M2 becomes from P and B, and r] 2-4 for 0-2p).

[Claim 3] Positive active material according to claim 1 or 2 whose amounts of a chalcogen compound are per [1] Li-Mn system multiple oxide 100 weight section - 30 weight sections.

[Claim 4] The manufacture approach of the positive active material for lithium secondary batteries characterized by heating positive active material according to claim 1 to 3 at 200-900 degrees C according to the mixed state of a chalcogen compound and a Li-Mn system multiple oxide.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the positive active material and its manufacture approach for lithium secondary batteries especially about positive active material and its manufacture approach.

[0002]

[Description of the Prior Art] Generally the lithium secondary battery is attracting attention all the more because it is excellent in the electromotive force list in respect of energy density, it is the purpose which develops a product with still higher practicality, and various kinds of improvement researches are made wholeheartedly in the field. Improvement research of the positive active material for these cells is also the one [important]. As positive active material, instead of multiple oxides, such as a conventional lithium and conventional Co, and nickel, it excels in safety more, and Li-Mn system multiple oxides abundant also in resource are proposed recently, and it is also known that a lithium secondary battery (4V class and 3V class) will be obtained depending on the content of Li in this multiple oxide.

[0003] If it furthermore uses permuting some manganese in a Li-Mn system multiple oxide by boron, i.e., a Li-Mn-B ternary system multiple oxide, according to JP,4-237970,A, it is known that the charge-and-discharge capacity of a cell will increase.

[0004] However, according to research of this invention persons, when the above-mentioned Li-Mn-B ternary system multiple oxide is used as positive active material of a nonaqueous electrolyte lithium secondary battery, there is a problem which is not enough.

[0005]

[Problem(s) to be Solved by the Invention] This invention aims at providing with the manufacture approach the positive-active-material list by which the cycle property of charge and discharge, especially the cycle property under high temperature have been improved in view of the above.

[0006]

[Means for Solving the Problem] This invention has the following description.

(1) Positive active material for lithium secondary batteries characterized by consisting of mixture of the chalcogen compound of at least 1 element and Li-Mn system multiple oxide which were chosen from the element group which consists of germanium, Sn, Pb, In, Sb, Bi, and Zn.

(2) The above whose chalcogen compound is $\text{Li}_r \text{M1M2p O}_q$ ($0.5-1.5q$ are [at least 1 element chosen from the group to which M1 consists of germanium, Sn, Pb, In, Sb, Bi, and Zn here, at least 1 element chosen from the group which M2 becomes from P and B, and r] 2-4 for 0-2p) (1) Positive active material of a publication.

(3) The above whose amounts of a chalcogen compound are per [1] Li-Mn system multiple oxide 100 weight section - 30 weight sections (1) Or (2) Positive active material of a publication.

(4) Above (1) - (3) The manufacture approach of the positive active material for lithium secondary batteries characterized by heating the positive active material of a publication at 200-900 degrees C to either according to the mixed state of a chalcogen compound and a Li-Mn system multiple oxide.

[0007]

[Function] The technical problem of this invention is solved by using the specific thing chosen from various compounds, i.e., the above-mentioned chalcogen compound, as mixture with a Li-Mn system multiple oxide. The operation been stable thru/or normalized by the device in which nothing and a chalcogen compound describe the function as positive active material of a Li-Mn system multiple oxide below for the function as the usual positive active material that the Li-Mn system multiple oxide in this mixture is the same is made.

[0008] The Li-Mn system multiple oxide which may function as positive active material is polycrystal powder, and according to research of this invention persons, generally, it has structure defective parts, such as many crystal defects and a closed opening, on the front face of this powder. Various side reaction other than an original cell reaction, especially an interface reaction are caused in the case of the charge and discharge of a cell, and such a structure defective part checks a normal cell reaction. As this interface reaction, it is the elution to the inside of the nonaqueous electrolyte of the manganese ion according to this ununiformity-izing to the ununiformity-ized list of crystalline degradation of an active material front face based on the interaction of a structure defective part and nonaqueous electrolyte, and the manganese ion in an active material crystal etc.

[0009] On the other hand, if a specific chalcogen compound is made to live together in this Li-Mn system multiple oxide, the side reaction, especially the interface reaction in the above-mentioned structure defective part of a Li-Mn system multiple oxide will be controlled. Although the detailed device of the control is not yet certain, it is thought that it is because a chalcogen compound covers and protects the above-mentioned crystal defect section, and it is filled up with a closed opening and an interface reaction is controlled thru/or prevented. In addition, even if a specific chalcogen compound is filled up with above-mentioned covering and the above-mentioned closed opening of the crystal defect section, it does not have a bad influence on insertion/elimination reaction of the lithium in the Li-Mn system multiple oxide as positive active material in practice. Although the specific chalcogen compound used by this invention will have the difference of extent, since it has generally quite good lithium ion conductivity and electronic conductivity according to the class as the reason, this invention persons think.

[0010] In this invention, although the above-mentioned operation is shown only by a chalcogen compound being simply mixed with a Li-Mn system multiple oxide, as the manufacture approach of this invention shows, the mixture of high performance can be further obtained by mixing them by specific high temperature. It is considered for covering and restoration of a Li-Mn system multiple oxide of a structure defective part with a chalcogen compound to progress much more certainly by mixing by specific high temperature as the reason.

[0011]

[Embodiment of the Invention] As a positive-active-material slack Li-Mn system multiple oxide in this invention, in the field, it is conventionally well-known, or the various things currently used serve as a candidate for use. For example, what has the spinel mold crystal structure and the non-spinel mold crystal structure which are shown by the following general formula (1) and (2) is illustrated.

$\text{Li}_x \text{MnO}_2$ (1) $\text{Li}_x \text{M}_3 \text{O}_4$ (2) In a general formula (1), it is $0.05 \leq x \leq 1.2$, especially $0.1 \leq x \leq 1.1$ here, and is each range of $0.01 \leq x \leq 1.5$, especially $0.05 \leq x \leq 1.1$ in a general formula (2). In a general formula (2), M3 is Mn at least. That is, M3 may be Mn independent and may be compound with elements other than Mn and Mn. As these elements other than Mn, they are Li and two groups (based on a new group display.) of the periodic table. It is below the same. It is the transition-metals element of 13 groups and 14 groups' type metallic element and four groups, eight groups, nine groups, and ten groups etc. Above all, Li, Mg, aluminum, nickel, Sn, etc. are desirable. Although, as for elements other than these Mn, two or more sorts may be contained in coincidence, as for especially the sum total molar quantity, considering as 0.2 mols or less is desirable 0.4 mols or less per one mol of Mn. as the desirable example of the Li-Mn system multiple oxide shown in a general formula (2) -- LiMn_2O_4 , $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$, and $\text{LiMn}_{1.95}\text{Mg}_{0.05}\text{O}_4$ -- 4, $\text{LiMn}_{1.95}\text{aluminum}_{0.05}\text{O}_4$, $\text{LiMn}_{1.95}\text{nickel}_{0.05}\text{O}_4$, $\text{LiMn}_{1.95}\text{Sn}_{0.05}\text{O}_4$, and $\text{LiMn}_{1.92}\text{nickel}_{0.03}\text{Sn}_{0.05}\text{O}_4$ etc. -- it is. Furthermore as a Li-Mn system multiple oxide, you may be a single compound, or may be two or more sorts of mixture.

[0012] The chalcogen compound of at least 1 element chosen from the element group which consists of germanium, Sn, Pb, In, Sb, Bi, and Zn as a chalcogen compound is used. This chalcogen compound may be a compound which contains other elements besides the compound which consists of at least 1 element chosen from the element group which consists of germanium, Sn, Pb, In, Sb, Bi, and Zn, two or more elements and one element of chalcogen (O, S, Se, Te, etc.), or two elements or more. The chalcogen compound which consists of at least 1 element chosen from the group which consists of Sn, Pb, In, and Sb from the point of discharge capacity also in the inside of the positive active material at the time of charge and discharge] in and out since electronic conduction nature is high and Li ion conductivity is high, consequently the charge-and-discharge cycle property of a cell becomes good, the multiple oxide shown by the following general formula (3) is desirable.

$\text{Li}_r \text{M}_1 \text{M}_2 \text{p O}_q$ (3)

At least 1 element chosen from the group to which M1 consists of germanium, Sn, Pb, In, Sb, Bi, and Zn here, at least 1 element chosen from the group which M2 becomes from P and B, and r are [0.5-1.5q of 0-2p] 2-4.

[0013] $\text{Li}_r \text{M}_1 \text{M}_2 \text{p O}_q$ As a desirable example, $\text{SnBO}_{2.8}$, $\text{SnP}_{0.5}\text{B}_{0.5}\text{O}_3$, and $\text{Li}_{0.2} \text{SnP}_{0.5}\text{B}_{0.5}\text{O}_3$, $\text{In}_{0.8} \text{Sn}$

0.2Pb0.5B0.5O₃ and Li_{0.3} In_{0.8} Sn 0.2Pb0.5B0.5O₃, Pb_{0.7} Sb_{0.3} BO_{3.4} and Li_{0.3} Pb_{0.7} Sb_{0.3} BO_{3.5}, germanium_{0.8} Bi 0.2Pb0.5B0.5O₃ and Li_{0.4}germanium_{0.8} Bi 0.2Pb0.5B0.5O_{3.2}, Sn_{0.8} Zn 0.2Pb0.5B0.5O_{3.3} and Li_{0.4} Sn_{0.8} Zn 0.2Pb0.5B0.5O_{3.5} etc. -- it is .

[0014] A Li-Mn system multiple oxide and a chalcogen compound are used as both mixture. In that case, to the amount of a Li-Mn system multiple oxide, the effectiveness of chalcogen compound use is scarce in too little [the amount of chalcogen compounds], and the concentration of the Li-Mn system multiple oxide which functions as the amount of chalcogen compounds being excessive as usual positive active material on the other hand falls, and it leads to the capacity fall of a cell. therefore, the amount of chalcogen compounds -- per [1] Li-Mn system multiple oxide 100 weight section - 30 weight sections -- it is 5 - 10 weight section preferably.

[0015] The mixture of a Li-Mn system multiple oxide and a chalcogen compound can be obtained by various approaches. Both powder, the impalpable powder which passes a desirable Tyler screen with an eye finer than 100 meshes or it 100%, and the impalpable powder which passes a Tyler screen with an eye finer than at least 200 meshes or it 100% especially are mixed enough mechanically most simply, and it is obtained. However, according to the manufacture approach of this invention described below, the mixture of high performance can be manufactured further.

[0016] In the manufacture approach of this invention, heat-treatment is performed after preparation with the compounding ratio which described above a powdered Li-Mn system multiple oxide and a powdered chalcogen compound. In addition, since there is a problem with which both will react and unite the mixture of high performance if too conversely high difficult to get, heating temperature is 200 degrees C or more, and it is desirable [temperature], when the temperature of heat-treatment is low to especially specifically consider as 400-700 degrees C 200-900 degrees C under the melting point of a Li-Mn system multiple oxide. In addition, where a Li-Mn system multiple oxide and a chalcogen compound are mixed good, it is necessary to perform the above-mentioned heat-treatment. However, the heat-treatment by this mixed state mixes both components beforehand under the room temperature, and, therefore, it is good for the approach of heat-treating mixing beforehand the approach which it supposes un-mixing, the method of performing mixing and heat-treatment for both non-mixed components to coincidence at the time of heat-treatment, or both components under the room temperature at the time of heat-treatment, and continuing mixing etc. The duration of heat-treatment is not based on the class of chalcogen compound, but is 3 - 10 hours especially for 1 to 20 hours.

[0017] Whether it may dissolve by the high temperature which requires the chalcogen compound used at the time of the above-mentioned heat-treatment or may deteriorate chemically to other chalcogen compounds, there is especially no problem. The impalpable powder which it is more desirable for both the Li-Mn system multiple oxides and chalcogen compounds that are used in the manufacture approach of this invention to be impalpable powder, and passes the Tyler screen of at least 100 meshes 100% preferably, and the impalpable powder which passes the Tyler screen of at least 200 meshes 100% especially are desirable.

[0018] The positive active material of this invention and the positive active material obtained from the manufacture approach of this invention are dealt with by the same approach as the conventional Li-Mn system multiple oxide, and is processed into the positive-electrode sheet for lithium secondary batteries. Moreover, with various kinds of negative-electrode sheets and usual separators using a negative-electrode active material, it can use and a lithium secondary battery can be manufactured.

[0019] Hereafter, while an example explains this invention to a detail further, the example of a comparison is also given and the remarkable effectiveness of this invention is shown.

[0020] LiMn 2O₄ of impalpable powder which passes the Tyler screen of 1-6330 meshes of examples The mixture which heat-treated for 5 hours and was subsequently heat-treated at the temperature (however, an example 4 has no heating) which shows after mixing under a room temperature and shows them in this table under atmospheric air by the ratio shown in Table 1 is ground using the one-sort slack SnP 0.5B0.5O₃ of a chalcogen compound. The positive active material of the impalpable powder which passes the Tyler screen of 330 meshes was obtained. in addition, the following Table 1 and 2 - 6 -- setting -- a chalcogen compound -- A -- moreover, LiMn 2O₄ etc. -- a lithium content manganese compound is displayed as B, respectively, and both operating weight ratio is shown.

[0021] Positive active material was obtained on the same approach and same conditions as examples 1-6 except having used Li_{0.2} SnP 0.5B0.5O₃ as an example 7 - 12 chalcogen compounds. Compounding ratio A/B and heat-treatment temperature are shown in Table 2.

[0022] Positive active material was obtained on the same approach and same conditions as examples 1-6 except having used Li_{0.3} In_{0.8} Sn 0.2Pb0.5B0.5O₃ as an example 13 - 18 chalcogen compounds. Compounding ratio A/B and heat-treatment temperature are shown in Table 3.

[0023] It is $\text{Li}_{0.4}\text{Pb}_{0.7}\text{Sb}_{0.3}\text{B}_{0.5}\text{P}_{0.5}\text{O}_{3.5}$ as an example 19 - 24 chalcogen compounds. Positive active material was obtained on the same approach and same conditions as examples 1-6 except having used. Compounding ratio A/B and heat-treatment temperature are shown in Table 4.

[0024] An example 25 - $30\text{LiMn}_2\text{O}_4$ It replaces with and is $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$. Positive active material was obtained on the same approach and same conditions as examples 1-6 except having used. Compounding ratio A/B and heat-treatment temperature are shown in Table 5.

[0025] LiMn_2O_4 used in the example of comparison 1 example 1 etc. It was used independently.

[0026] $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ used in the example of comparison 2 example 25 etc. It was used independently.

[0027] Each positive active material (impalpable powder with which all pass the Tyler screen of 330 meshes) of examples 1-30 and the examples 1-2 of a comparison was used, the positive-active-material 92 weight section, the acetylene black 3 weight section, the polyvinylidene fluoride 5 weight section, and the N-methyl-2-pyrrolidone 70 weight section were mixed, and it considered as the slurry. This slurry is applied on aluminium foil, and it dries, and is 20 mg/cm². The positive-electrode sheet which has positive active material was produced. Adhesion opposite of each positive-electrode sheet and Li foil which were obtained in this way is carried out through a porosity polyethylene separator, and it is one mol [per 1l. (the rate of a mixed volume ratio is 1:1) of mixed solvents] LiPF₆ of ethylene carbonate and ethyl methyl carbonate. The solution which comes to dissolve was used as the electrolytic solution, this was sunk in between the above-mentioned positive-electrode sheet and Li foil, and the lithium secondary battery of closed mold was produced.

[0028] After measuring about each lithium secondary battery from the first time trial of the charge-and-discharge cycle test method which shows the initial discharge capacity in those room temperatures (23 degrees C **3 degrees C) below, the charge-and-discharge cycle property in 30 cycle deed and this temperature was evaluated for the same charge-and-discharge cycle trial in the 60-degree C thermostat. The result is shown in Tables 1-6. Those tables show that the lithium secondary battery which used the positive active material of each example of this invention is extremely superior to the lithium secondary battery which used the positive active material of the example of a comparison in the charge-and-discharge cycle property in 60 degrees C.

[0029] Charge-and-discharge cycle test method: Area 1cm² of a positive-electrode sheet It charges for 5 hours under the constant current and the constant voltage of 4.3V of 1mA of hits, and, subsequently is 2 an area of 1cm² of a positive-electrode sheet. It is made to discharge until terminal voltage is set to 3V under constant current of 0.5mA of hits, and charge and discharge are stopped after this for 1 hour. It repeats 30 times by making a pause into 1 cycle at the charge-and-discharge list of the more than performed at 60 degrees C. The discharge capacity of 30 cycle eye computes quantity of electricity (mA-H) from a discharge current value and a charging time value, and obtains discharge capacity (mA-H/g) from the weight (g) of the positive active material contained in the lithium secondary battery. In addition, in Table 1 - 6, the value (%) shown in a parenthesis after the discharge capacity value of 30 cycle eye is, the ratio (%), i.e., the capacity retention, of discharge capacity of 30 cycle eye to initial discharge capacity.

[0030]

[Table 1]

	A/B (重量 比)	加熱処理 温度 (°C)	放電容量 (mAh/g)	
			初期	30 サイクル目
実施例 1	5/ 100	600	115.7	100.0 (86.4%)
実施例 2	10/ 100	500	110.2	101.5 (92.1%)
実施例 3	30/ 100	500	94.3	85.3 (90.5%)
実施例 4	10/ 100	加熱無し	112.8	73.5 (65.2%)
実施例 5	10/ 100	200	112.5	79.1 (70.3%)
実施例 6	10/ 100	700	95.4	77.1 (80.8%)

[0031]

[Table 2]

	A/B (重量 比)	加熱処理 温度 (°C)	放電容量 (mAh/g)	
			初期	30 サイクル目
実施例 7	5/ 100	600	118.3	103.5 (87.5%)
実施例 8	10/ 100	500	114.5	105.1 (91.8%)
実施例 9	30/ 100	500	98.7	91.2 (92.4%)
実施例 10	10/ 100	加熱無し	116.4	78.3 (67.3%)
実施例 11	10/ 100	200	115.2	88.6 (76.9%)
実施例 12	10/ 100	700	99.3	89.6 (90.2%)

[0032]

[Table 3]

	A/B (重量 比)	加熱処理 温度 (°C)	放電容量 (mAh/g)	
			初期	30 サイクル目
実施例 13	5/ 100	600	119.0	107.6 (90.4%)
実施例 14	10/ 100	500	114.2	107.6 (94.1%)
実施例 15	30/ 100	500	99.1	92.8 (93.6%)
実施例 16	10/ 100	加熱無し	115.8	82.8 (71.5%)
実施例 17	10/ 100	200	115.0	94.6 (82.3%)
実施例 18	10/ 100	700	102.4	88.3 (86.2%)

[0033]

[Table 4]

	A/B (重量 比)	加熱処理 温度 (°C)	放電容量 (mAh/g)	
			初期	30 サイクル目
実施例 19	5/ 100	600	114.6	96.3 (84.0%)
実施例 20	10/ 100	500	108.5	98.0 (90.3%)
実施例 21	30/ 100	500	92.5	83.9 (90.7%)
実施例 22	10/ 100	加熱無し	110.6	70.9 (64.1%)
実施例 23	10/ 100	200	108.3	75.8 (70.0%)
実施例 24	10/ 100	700	94.1	80.7 (85.8%)

[0034]

[Table 5]

	A/B (重量 比)	加熱処理 温度 (°C)	放電容量 (mAh/g)	
			初期	30 サイクル目
実施例 2 5	5/ 100	600	108.4	98.1 (90.5%)
実施例 2 6	10/ 100	500	103.2	100.2 (97.1%)
実施例 2 7	30/ 100	500	88.1	84.8 (96.3%)
実施例 2 8	10/ 100	加熱無し	106.8	78.2 (73.2%)
実施例 2 9	10/ 100	200	105.2	82.5 (78.4%)
実施例 3 0	10/ 100	700	100.6	91.1 (90.6%)

[0035]

[Table 6]

	A/B (重量 比)	加熱処理 温度 (°C)	放電容量 (mAh/g)	
			初期	30 サイクル目
比較例 1	—	—	120.5	39.5 (32.8%)
比較例 2	—	—	114.1	71.1 (62.3%)

[0036]

[Effect of the Invention] As compared with the conventional lithium secondary battery which uses a lithium manganese multiple oxide as positive active material, the lithium secondary battery which used the positive active material of this invention is extremely excellent in the charge-and-discharge cycle property, especially the charge-and-discharge cycle property under the high temperature around 60 degrees C, and excellent also in the stability of preservation at the time of moreover saving under ordinary temperature or the high temperature around 60 degrees C with a charge condition. Therefore, the positive active material of this invention is suitable for manufacture of the long lasting lithium secondary battery for various kinds of electrical machinery and apparatus division portables.

[Translation done.]